PATENT SPECIFICATION

NO DRAWINGS

1,105,565

Inventors: LEONARD TURNER and CHRISTOPHER PATRICK CADMAN BRADSHAW

Date of filing Complete Specification: 16 March, 1966.

Application Date: 20 May, 1965. *No. 21368/65.*

Complete Specification Published: 6 March, 1968.

1,105,565

Index at acceptance:—C5 E(7B2A1, 7B2A2, 7B2Y, 8A5A2, 8A5Y, 8A8A3, 8A8B1, 8A8B2, 8A8Y)

Int. Cl.:—C 07 c 3/10, C 07 c 13/02

COMPLETE SPECIFICATION

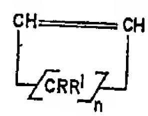
Polymerisation Process

We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for the production of polymers of cyclo-olefins and to the polymers themselves.

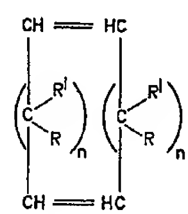
According to one aspect of the present invention there is provided a process for the production of a cyclic polymer of one or more cyclo-olefins of general formula

(I)

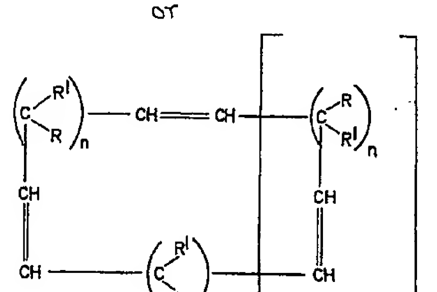


wherein R and R′ which may be the same or different are alkyl, aryl, alkaryl or cyclo-alkyl groups or hydrogen atoms and n is an integer not less than 5 and preferably not more than 18, the polymer being of structure

(II)



or



(III)

wherein R, R′ and n are as hereinbefore defined and need not have the same value in each case, and m is an integer, the process comprising contacting one or more cyclo-olefins with a disproportionation catalyst under polymerising conditions.

By disproportionation catalyst we mean a substance which can be used to promote the disproportionation of linear olefins.

By polymers we mean compounds the molecules of which are prepared by the union of two or more molecules of the same or different compounds. Thus dimers and copolymers are within the scope of the term polymers.

The catalysts used in the present process are olefin disproportionation catalysts, that is to say catalysts which will effect the disproportionation of single acyclic olefins into olefins having a higher and lower carbon number than the initial olefin. Catalysts which are known to effect such disproportionation and are therefore suitable for use in the present process are mixtures of molybdenum oxide and alumina, preferably containing cobalt oxides and optionally containing minor amounts of alkali metal or alkaline earth metal ions; molybdenum or tungsten carbonyls supported on alumina, silica or silica/alumina and tungsten oxides supported on alumina. In addition, our copending Application 36722/64, 50985/64 (cognate) (Serial No. 1,054,864), discloses a process for the disproportionation of olefins over a catalyst comprising rhenium heptoxide supported on alumina.

All these catalysts are activated before use by subjecting them to a thermal treatment, either in a stream of inert gas such as ntirogen, carbon dioxide or helium, or preferably in a stream of air or oxygen followed by a final treatment in an inert gas. Suitably the catalysts are heated in air at a temperature in the range 300° to 900°C for 1 minute to 20 hours and then under similar conditions in an inert gas such as nitrogen.

The most preferred catalyst consists solely of rhenium heptoxide and alumina.

Suitable methods for preparing the most preferred catalyst are disclosed in our copending Applications 17221/65 (Serial No. 1,105,563), 17222/65 (Serial No. 1,105,564), 31458/65 (Serial No. 1,089,956), and 5191/66 (Serial No. 1,103,976).

Suitable cyclo-olefins include cyclo-octene and cyclo-dodecene.

The conditions under which the process is carried out may vary with the composition of the feed and the desired products.

Reaction temperatures are suitably in the range −20° to +250°C, preferably in the range 20° to 150°C. Polymerisation is preferably effected at such a temperature that the reactant is in the liquid phase.

Pressure may be atmospheric, superatmospheric or subatmospheric.

Suitable olefin/catalyst weight ratios are in the range 1:1 to 5000:1.

If desired, the process may be effected in the presence of an inert diluent, for example a liquid hydrocarbon or halogenated hydrocarbon.

Reaction times may vary, and generally the shorter the time of contact of the olefin with the catalyst the lower will be the molecular weight of the resulting polymer.

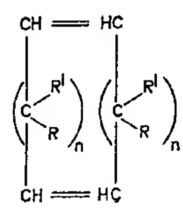
The production of dimers is favoured by a process which comprises refluxing the monomer (s) in Soxhlet-type equipment, the catalyst being contained in the thimble.

The production of higher molecular weight polymers is favoured by refluxing the monomer (s) in the presence of the catalyst.

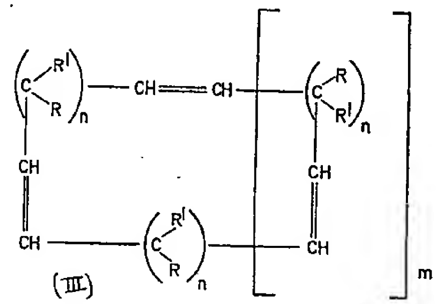
The higher molecular weight polymers are colourless amorphous materials which may be vulcanised by conventional methods to form elastomers.

According to another aspect of the present invention there is provided a polymer of structure

(II)



or



(III)

wherein R, R′, m and n are as hereinbefore defined.

The invention is illustrated by the following examples.

EXAMPLE 1

Polymerisation of cyclo-octene

"Actal" alumina (20 g) of particle size 30—60 BSS was impregnated with ammonium perrhenate (3.6 g) in water (60 ml), stirred and evaporated to dryness on a water-bath, dried at 110°C for 12 hours, and finally activated in a stream of dry air for 1 hour at 580°C then dry nitrogen for 1.5 hours at 580°C. "Actal" is a Registered Trade Mark.

Dry cyclo-octene (100 ml) was added to 30 ml of the above catalyst, stirred, and heated to the boiling point of the olefin (143°C). The mixture rapidly became viscous and 4 successive portions of 50 ml of the olefin were added at equal intervals over a period of 4 hours. The organic product was removed in 3 litres of boiling *n*-heptane, most of the solvent and excess olefin were removed by distillation at normal pressure, and volatile matter was finally eliminated at 150°C, 0.1 mm pressure. A rubbery, colourless material (102 g, 40% by wt of feed) was obtained, of number-average molecular weight 650, corresponding to an average of 5.8 monomer units per polymer molecule. The infra-red spectrum of this product was consistent with the presence of one double-bond per 8 carbon atoms i.e. with the structure of general formula III for the polymer where m = 4, n = 6.

EXAMPLE 2

Polymerisation of cyclo-dodecene

Cyclo-dodecene (30 ml) diluted with *n*-heptane (30 ml) was heated under reflux for 3 hours with the catalyst (10 ml) as made in Example 1. A white, waxy solid precipitated, and was recovered as in Example 1. The yield was 20.4 g (68% by wt. on feed) and the number-average molecular weight 970, corresponding to 5.8 monomer units per polymer molecule. The polymer contained C 86.4 and H 13.6% by wt. (required for $(C_{12}H_{22})_n$, C 86.8 and H 13.2 per cent). The infra-red spectrum was consistent with an unbranched ring compound with double-bonds (mainly trans) at intervals of about 12 carbon atoms, i.e. the polymer had the structure of general formula III where m = 4, n = 10.

EXAMPLE 3

Preparation of cyclo-hexadecadiene

The catalyst (20 ml) as prepared in Example 1 was placed in a Soxhlet thimble and cyclo-octene (30 ml) diluted with *n*-hexane (60 ml) boiled in the flask of a normal Soxhlet apparatus for 12 hours so that the refluxing liquid contacted the catalyst. The solvent and excess cyclo-octene were distilled off at atmospheric pressure and the residue distilled in vacuo to yield 2 g (6% by wt. on feed) of a colourless liquid at 90—110°C, 0.1 mm Hg pressure.

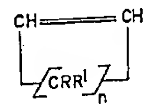
GLC analysis showed that this product contained 95 per cent of a compound of carbon number about 16.

On hydrogenation over a PtO_2 catalyst there was obtained a saturated product of molecular weight 224 by mass spectrometry. The infra-red spectrum showed that no double-bonds were present, that no methyl groups were present, and that there was no branching of the carbon chain. Examination of the reduced product by nuclear

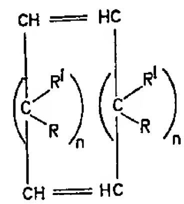
magnetic resonance showed that the substance contained only equivalent CH_2 groups. It must therefore have been cyclo-hexadecane ($C_{16}H_{32}$, molecular weight 224). In the production of this saturated hydrocarbon, hydrogen equivalent to 2 double bonds per molecule was taken up by the original dimer which must therefore be cyclo-hexodecadiene.

WHAT WE CLAIM IS:—

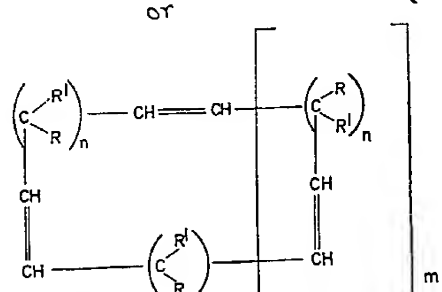
1. A process for the production of a cyclic polymer of one or more cyclo-olefins of general formula

(I) 

wherein R and R′, which may be the same or different, are alkyl, aryl, alkaryl or cyclo-alkyl groups or hydrogen atoms, and n is an integer not less than 5 and preferably not more than 18, the polymer being of structure

(II) 

or



(III)

wherein R, R′ and n are as hereinbefore defined and need not have the same value in each case, and m is an integer, the process comprising contacting one or more cyclo-olefins with a disproportionation catalyst as hereinbefore defined under polymerising conditions.

2. A process according to claim 1, wherein the catalyst consists solely of rhenium heptoxide and alumina.

3. A process according to either of the preceding claims, wherein the cyclo-olefin is cyclo-octene or cyclo-dodecene.

4. A process according to any of the preceding claims, wherein polymerisation is effected at a temperature in the range $-20°$ to $+250°C$.

5. A process according to claim 4, wherein polymerisation is effected at temperature in the range 20° to 150°C.

6. A process according to any of the preceding claims, wherein polymerisation is effected at such a temperature that the reactants are in the liquid phase.

7. A process according to any of the preceding claims, wherein the olefin/catalyst weight ratio is in the range 1 : 1 to 5000 : 1.

8. A process according to any of the preceding claims, wherein polymerisation is effected in the presence of an inert diluent.

9. A process according to claim 8, wherein the diluent is a normally liquid hydrocarbon or halogenated hydrocarbon.

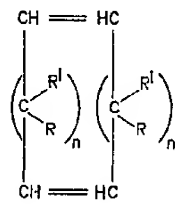
10. A process according to any of the preceding claims for the production of dimers which comprises refluxing the monomer(s) in Soxhlet-type equipment, the catalyst being contained in the thimble.

11. A process according to any of claims 1—9 for the production of higher molecular weight polymers which process comprises refluxing the monomer (s) in the presence of the catalyst.

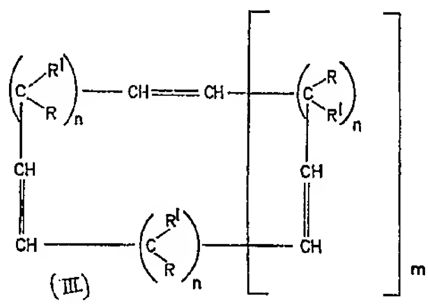
12. A process according to claim 1 as hereinbefore described with reference to the Examples.

13. A polymer of structure

(II)



or



(III)

wherein R, R′, m and n are as hereinbefore defined.

14. Polymers whenever prepared by a process according to any of claims 1—12.

J. WOOLARD,
Agent for the Applicants,
Chartered Patent Agent.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.